Alumina-supported In$_2$O$_3$, Ga$_2$O$_3$ and B$_2$O$_3$ catalysts for lean NO$_x$ reduction with dimethyl ether

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ABSTRACT

Alumina-supported In$_2$O$_3$, Ga$_2$O$_3$ and B$_2$O$_3$ were investigated as catalysts for lean NO$_x$ reduction with DME as reducing agent and compared to pure Al$_2$O$_3$ and In$_2$O$_3$. The In$_2$O$_3$-promoted alumina catalysts showed the highest NO$_x$ conversion at low temperatures, although with a narrow temperature window. Pure In$_2$O$_3$, on the other hand, was inactive for NO$_x$ reduction with DME. The Ga$_2$O$_3$- and B$_2$O$_3$-promoted alumina catalysts gave the highest NO$_x$ conversion at higher temperatures, showed a temperature window similar to pure alumina, but were less sensitive to H$_2$O inhibition. Possible reasons for these observations are discussed.

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Introduction

The concern for global warming and energy supply has induced a large increase in research activities and investments in production of alternative fuels. This is of particular importance in the transport sector where virtually all of the energy (95%) comes from oil based fuels [1]. For the diesel engine, dimethyl ether (DME) is a potent alternative fuel, with its high cetane number and virtually soot free combustion [2,3]. DME can be produced from fossil feedstock such as natural gas and coal as well as from biomass. If it is produced from biomass it offers a high potential for low CO$_2$ emissions combined with a high well-to-wheel energy efficiency [4,5].

Although the combustion of DME provides the possibility to reach very low NO$_x$ emissions compared to diesel, aftertreatment measures could be a cost effective alternative to reach the toughest emission legislation levels. As the DME engine operates under lean conditions the ordinary three-way catalyst is not suitable for NO$_x$ reduction. The NO$_x$ aftertreatment technologies that can be used under these conditions are the periodically operating lean NO$_x$

trap (LNT) or the continuous selective catalytic reduction (SCR) by ammonia or hydrocarbons. The main drawbacks with the LNT are that it requires expensive noble metal catalysts and complicated engine control to achieve periodic enrichment of the exhaust in order to regenerate the trap. NH$_3$-SCR on the other hand requires that an additional reductant, ammonia or urea, is carried onboard. Hydrocarbon-SCR or in this case DME-SCR, utilizing the vehicle fuel as reducing agent, would be a simpler alternative to implement. The catalysts used for this process are generally called lean NO$_x$ catalysts (LNC). Earlier studies have shown that conventional diesel LNCs such as Cu-ZSM-5 or Ag/Al$_2$O$_3$ give very low NO$_x$ reduction with DME as reducing agent [6–8]. This study has been focused on investigating alternative catalysts more efficient at reducing NO$_x$ with DME. A limited amount of studies can be found in the literature on HC-SCR with DME as reductant [8–21]. The catalysts studied have been either pure Al$_2$O$_3$, Al$_2$O$_3$-supported noble metals (Ag) or transition- or post-transition metal oxides (V, Co, Mo, Ga, Sn), or ion-exchanged (H, Na, Ag, Pd) zeolites. Pure alumina showed considerable activity for DME-SCR at higher temperatures (above 300–350 °C) [8,12]. However, for the diesel engine application it is desirable to lower the temperature where the catalyst becomes active. A recent patent claimed that Al$_2$O$_3$ promoted with indium oxide was active at lower temperatures than pure Al$_2$O$_3$ with DME [22]. Similar behaviour has been demonstrated with propene and ethanol as reducing agents [23–26].

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The purpose of this study was to investigate and compare the DME-deNO$_x$ activity and characteristics of oxides of the group 13 elements of the periodic table. A series of catalysts consisting of γ-Al$_2$O$_3$ promoted with In$_2$O$_3$, Ga$_2$O$_3$, or B$_2$O$_3$ at different loadings was thus compared to pure γ-Al$_2$O$_3$ in the SCR reaction with DME. Earlier studies on alumina promoted with In$_2$O$_3$, Ga$_2$O$_3$ or B$_2$O$_3$, found in the literature, were performed with a variety of reducing agents including alkanes, alkenes, and alcohols [23–39]. Only one of these studies included the use of DME as reductant; Miyahara et al. [27] investigated the SCR of NO with C$_1$–C$_3$ reductants over Ga$_2$O$_3$/Al$_2$O$_3$ catalysts. They reported a maximum NO conversion of about 35% with DME, compared to 90–100% with alkanes or alkenes, under dry conditions. However, in contrast to alkanes and alkenes, the NO conversion with DME was almost unaffected by the addition of water. They explained this by the fact that the dissociative adsorption of DME was not inhibited by water. Similar behaviour in the presence of water has also been reported with alcohols in another study [30]. To our knowledge, the NO$_x$ reduction with DME has not previously been reported as a comparative study between In$_2$O$_3$-, Ga$_2$O$_3$-, and B$_2$O$_3$-promoted Al$_2$O$_3$ catalysts.

Experimental

Catalyst preparation

A commercial γ-Al$_2$O$_3$ powder (Puralox® SBa200, Sasol) was used for the catalyst preparation. The promoted catalyst samples were prepared by incipient wetness impregnation of this γ-Al$_2$O$_3$ with aqueous solutions of indium(III)nitrate (Aldrich, 99.9% metals basis), gallium(III)nitrate (Aldrich, 99.9% metals basis) or boric acid (Aldrich, 99.999% metals basis). The concentration of these solutions was varied to obtain powders with four different loadings of each metal. To enable the comparison between the different metals, their loadings were based on equal molar content. After impregnation the powders were freezed in liquid nitrogen, freeze dried overnight, and calcined in air at 550 °C for 2 h. Pure In$_2$O$_3$ powder was obtained from Aldrich (Indium(III)oxide nanopowder, <100 nm). The catalyst powders were then mixed in a weight ratio of 4:1 with a binder (Disperal® P2, Sasol for the Al$_2$O$_3$-based samples and Bindzil® colloidal silica 30NH$_3$/220, Eka Chemicals for the In$_2$O$_3$ sample), suspended in deionised water to obtain a slurry, and washcoated onto cordierite monoliths. The monolith samples had a length of 20 mm, a diameter of 20 mm, and a cell density of 400 cpsi (cells per square inch). In the washcoating procedure the monolith was immersed in the slurry and excess liquid was removed by gently blowing air through the channels and on the outside of the monolith sample. The sample was then dried in air at 90 °C and calcined in air at 600 °C for 2 min. This procedure was repeated until the weight of the washcoat corresponded to approximately 20% of the total sample weight. Finally, the monoliths were calcined in air at 550 °C for 2 h and were then ready for reactor tests. The final weight of the washcoat of the monoliths after calcination was measured to be 0.73 ± 0.03 g.

Catalyst characterisation

Surface area, pore volume and pore size distribution measurements were performed on the catalyst powders using a Micromeritics Tristar® 3000 analyser. The samples were outgassed under vacuum at 225 °C overnight before nitrogen adsorption–desorption isotherms were collected at −196 °C. The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) equation, and specific pore volume and pore diameter were obtained using the Barrett–Joyner–Halenda (BJH) model [40,41].

X-ray powder diffraction patterns were obtained with a Bruker AXS D8 ADVANCE diffractometer using monochromatic Cu K$_{\alpha 1}$ radiation. Data were collected in the 2θ range 10–80°, which was scanned at a rate of 0.04°/2 s.

Catalytic activity measurements

The catalytic activity tests were performed in a horizontally mounted quartz tube flow reactor. Thermocouples were used to measure the temperature in the gas stream before the catalyst as well as inside a centre channel of the monolith sample. The inlet gas tubes and the reactor wall were heated by metallic heating coils. The set temperature for the reactor wall was varied during the experiments, whereas that for the inlet gas tubes was set to 100 °C. Mass flow controllers (Bronkhorst Hi-Tech) for gases and distilled water were used to regulate the flow composition into the reactor. The reactor outlet gas was continuously analysed with a frequency of 1 Hz using a MKS Multigas^{TM} 2030 FTIR analyser.

Similar experiments were performed on all catalysts included in the study and also in the empty reactor to study the conversion of DME. All tests were initiated with a conditioning of the catalyst at 550 °C for 30 min in 8% O$_2$ in Ar. The total gas flow in all tests was 3500 ml/min, giving a space velocity of 33,400 h^{-1} based on the monolith volume. After conditioning, the NO reduction activity was evaluated during temperature ramps from 550 to 200 °C at 10 °C/min. In the first ramp the feed gas consisted of 500 ppm NO, 1000 ppm DME, 8% O$_2$, and Ar as balance. Similar ramps were also performed with 5% H$_2$O added to the feed, with 5% H$_2$O and doubled DME concentration (2000 ppm), or with 500 ppm NO$_2$ instead of NO. Finally, activity measurements were performed during steady-state conditions at temperatures between 550 and 250 °C in a feed gas consisting of 500 ppm NO, 1000 ppm DME, 8% O$_2$, 5% H$_2$O, and Ar as balance. Measurements were made after conditions had been allowed to stabilise for 15 min at each temperature.

In the evaluation of the results, the conversion of NO$_x$ and DME is defined as $1 - [X]_{out}/[X]_{in}$ and the yield of CO, CO$_2$, formaldehyde, and formic acid as $[X]_{out}/2[DME]_{in}$, were X denotes the component in question. The concentrations of the different gases were calculated by the FTIR instrument based on calibration curves using N$_2$ as carrier gas. In this study, however, Ar was used as carrier gas. Differences in the measured concentrations depending on the carrier gas are less than 10%. The reported concentrations of NO, NO$_2$, DME, CO, and CO$_2$ were compensated for these differences by separate calibrations.

Results and discussion

Characterisation of catalysts

Table 1 shows the nominal elemental composition of the different catalyst powder samples as well as their BET surface area, pore volume, and average pore diameter. The specific surface area decreased with increasing content of In$_2$O$_3$ or Ga$_2$O$_3$, where the difference was especially large for the In$_2$O$_3$-loaded materials. For the Ga$_2$O$_3$-loaded materials the difference can be attributed to the higher atomic mass of Ga compared to Al. This becomes obvious when comparing the surface area per gram of Al$_2$O$_3$ in the materials. For the In$_2$O$_3$/Al$_2$O$_3$ materials there is a decrease in the specific surface area even if the effect of the atomic mass difference is taken into account. The specific surface area of the B$_2$O$_3$-loaded materials was similar to that of pure Al$_2$O$_3$. The pure In$_2$O$_3$ powder had a low specific surface area, but again, the much higher molar mass of In$_2$O$_3$ (about 2.7 times) compared to Al$_2$O$_3$ must be taken into account. The pore volume and pore diameter decreased with increasing content of In$_2$O$_3$, Ga$_2$O$_3$, or B$_2$O$_3$. The pure In$_2$O$_3$

Table 1
Physical properties of the catalysts.

Catalyst	Nominal metal loading (wt%)		BET surface area (m^2 g^{-1} of sample)	BET surface area (m^2 g^{-1} of support)[a]	Pore volume (cm^3 g^{-1})	Average pore diameter (nm)
	M	M$_2$O$_3$				
Al$_2$O$_3$	0	0	198	198	0.503	8.21
1.2% In$_2$O$_3$/Al$_2$O$_3$	1.0	1.2	192	194	0.503	8.38
3.0% In$_2$O$_3$/Al$_2$O$_3$	2.5	3.0	190	195	0.490	8.23
6.0% In$_2$O$_3$/Al$_2$O$_3$	5.0	6.0	181	193	0.470	8.26
12% In$_2$O$_3$/Al$_2$O$_3$	10	12	166	189	0.430	8.17
In$_2$O$_3$	83	100	28.4	–	0.0965	14.0
0.82% Ga$_2$O$_3$/Al$_2$O$_3$	0.61	0.82	195	196	0.504	8.27
2.0% Ga$_2$O$_3$/Al$_2$O$_3$	1.5	2.0	194	198	0.497	8.25
4.1% Ga$_2$O$_3$/Al$_2$O$_3$	3.0	4.1	189	197	0.479	8.22
8.2% Ga$_2$O$_3$/Al$_2$O$_3$	6.1	8.2	184	200	0.454	8.08
0.30% B$_2$O$_3$/Al$_2$O$_3$	0.094	0.30	197	198	0.507	8.24
0.76% B$_2$O$_3$/Al$_2$O$_3$	0.24	0.76	199	200	0.509	8.14
1.5% B$_2$O$_3$/Al$_2$O$_3$	0.47	1.5	197	200	0.504	8.17
3.0% B$_2$O$_3$/Al$_2$O$_3$	0.94	3.0	196	202	0.493	8.09

[a] Based on the weight of the Al$_2$O$_3$ support only.

material had a lower pore volume and about twice the pore diameter compared to the Al$_2$O$_3$-based materials. If the difference in molar mass of In$_2$O$_3$ compared to Al$_2$O$_3$ is taken into account the pore volume of In$_2$O$_3$ is about half that of Al$_2$O$_3$. As will be apparent later, the small differences in surface area, pore volume, and pore diameter between the promoted and pure Al$_2$O$_3$ samples do not appear to play a major role for the NO$_x$ reduction as some of the catalysts with smaller pores showed the highest activity.

The X-ray diffractograms of the In$_2$O$_3$-, Ga$_2$O$_3$-, and B$_2$O$_3$-promoted alumina powders are compared to those of the pure γ-Al$_2$O$_3$ and In$_2$O$_3$ powders in Fig. 1. The pattern of the pure In$_2$O$_3$ material verified that it was in its cubic polymorph (PDF no. 00-006-0416, ICDD). For the high In$_2$O$_3$-loaded materials, i.e. 6.0 and 12% In$_2$O$_3$/Al$_2$O$_3$, peaks characteristic for both γ-Al$_2$O$_3$ and cubic In$_2$O$_3$ were observed. The peaks due to In$_2$O$_3$ increased with increasing In$_2$O$_3$ content. For the low In$_2$O$_3$-loaded samples, i.e. 1.2 and 3.0% In$_2$O$_3$/Al$_2$O$_3$, only peaks due to γ-Al$_2$O$_3$ and no peaks due to In$_2$O$_3$ were observed, most likely as a result of its low concentration in these materials. This is in agreement with results presented in the literature [28]. Regarding the Ga$_2$O$_3$- and B$_2$O$_3$-promoted alumina powders no peaks other than the ones due to γ-Al$_2$O$_3$ were observed even at the highest loadings, why only the patterns for 8.2% Ga$_2$O$_3$/Al$_2$O$_3$ and 3.0% B$_2$O$_3$/Al$_2$O$_3$ are shown in Fig. 1. This is in accordance with other XRD studies of samples with similar composition [29,42] and the fact that B$_2$O$_3$ is known to be a difficult substance to crystallise [43].
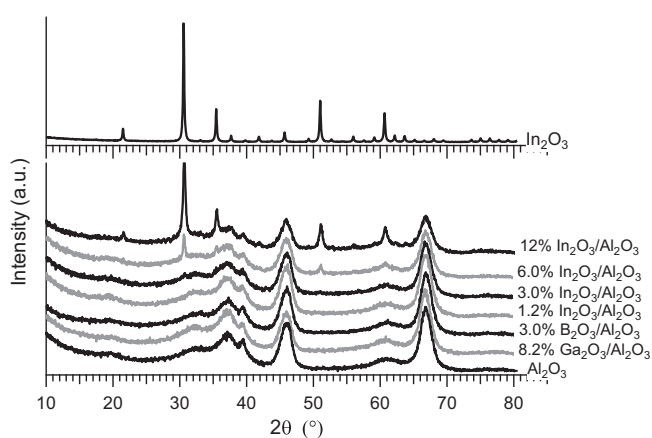

Fig. 1. XRD patterns for pure Al$_2$O$_3$ and In$_2$O$_3$, for the four In$_2$O$_3$/Al$_2$O$_3$ materials and for the Ga$_2$O$_3$/Al$_2$O$_3$ and B$_2$O$_3$/Al$_2$O$_3$ materials with the highest loading of Ga$_2$O$_3$ and B$_2$O$_3$, respectively.

Catalytic activity measurements under steady-state conditions

The steady state experiments were performed in order to assess general differences between the catalysts. The detailed behaviour of the catalysts, including by-product formation and temperature dependence, was studied during the temperature ramp experiments discussed in the following section.

Fig. 2 shows the conversion of NO$_x$ and DME over the In$_2$O$_3$-promoted Al$_2$O$_3$ catalysts compared to pure In$_2$O$_3$ and Al$_2$O$_3$ catalysts during steady-state at temperatures between 250 and 550 °C, in the presence of 5% H$_2$O and at an HC$_1$/NO$_x$-ratio of 4. The results show that In$_2$O$_3$-promoted Al$_2$O$_3$ and pure Al$_2$O$_3$ were active for NO$_x$ reduction with DME, whereas pure In$_2$O$_3$ was virtually inactive for this reaction in the temperature range studied. Similar results were reported by Maunula et al. [30] with propene as reductant. Comparing the results for the In$_2$O$_3$-promoted samples with the pure Al$_2$O$_3$ sample, the maximum NO$_x$ conversion increased and occurred at 350 °C instead of 450 °C as a result of In$_2$O$_3$ addition. The highest NO$_x$ conversion of 47% was observed for 1.2% In$_2$O$_3$/Al$_2$O$_3$, whereas for Al$_2$O$_3$ the maximum was only 31%. The influence of the In$_2$O$_3$ loading on NO$_x$ conversion was relatively low within the range studied. The maximum NO$_x$ conversion at 350 °C decreased slightly with higher In$_2$O$_3$ loading, but not proportionally. Increasing the loading of In$_2$O$_3$ from 1.2 to 12% gave only a difference of about 10%-units in NO$_x$ conversion. At 300 °C, however, the catalyst with highest In$_2$O$_3$ loading showed the highest NO$_x$ conversion. This observation will be analysed in more detail in the temperature ramp experiments. Above 400 °C, the pure Al$_2$O$_3$ catalyst showed the highest NO$_x$ conversion, whereas among the In$_2$O$_3$-loaded samples the 1.2% In$_2$O$_3$/Al$_2$O$_3$ catalyst was still the most active.

DME was converted at slightly higher temperature over the In$_2$O$_3$-promoted catalysts than over pure alumina at temperatures below 350 °C, although at 400 °C and above, DME was completely converted over all these catalysts. Pure In$_2$O$_3$ showed the lowest conversion of DME through the entire temperature range and the light-off for DME conversion occurred at higher temperature than for the other catalysts. In fact, over this catalyst DME was not completely converted even at 550 °C. With the exception of the pure In$_2$O$_3$, the catalyst with the highest In$_2$O$_3$ loading showed the lowest DME conversion at 300 °C and thus the highest selectivity for the DME-SCR reaction at that temperature, whereas at 350 °C the opposite trend is found.

At 300 °C neither pure In$_2$O$_3$ nor pure Al$_2$O$_3$ were able to reduce NO$_x$, whereas the four In$_2$O$_3$/Al$_2$O$_3$ catalysts were. In fact, when studying the gas composition after the pure In$_2$O$_3$ sample (not
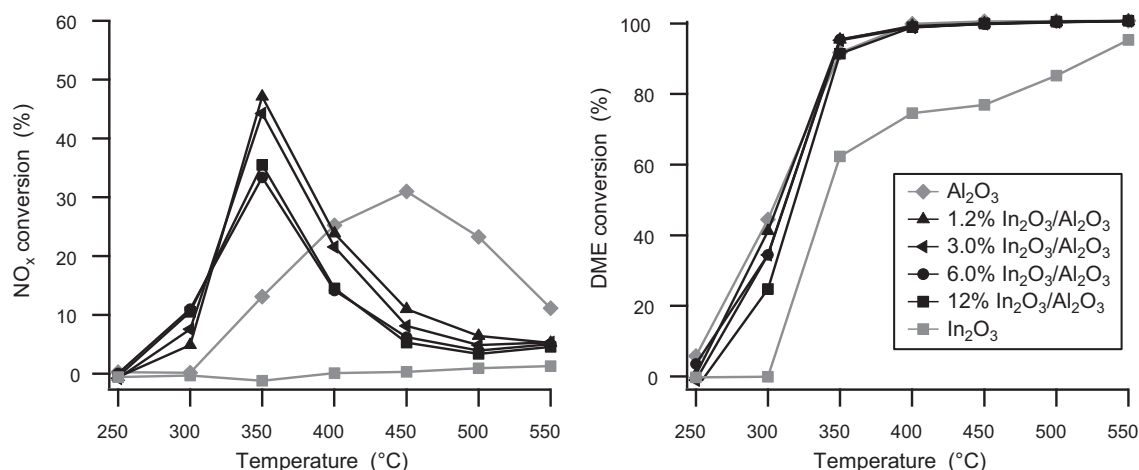
Fig. 2. Conversion of NO_x and DME during steady-state experiments with In_2O_3/Al_2O_3, pure In_2O_3 and pure Al_2O_3 catalysts. Gas feed contained 500 ppm NO, 1000 ppm DME, 5% H_2O, 8% O_2, and Ar as balance. Space velocity = 33,400 h^{-1}.

shown), neither NO nor DME were affected at 300 °C over this catalyst alone. This shows that the In_2O_3 and Al_2O_3 sites need to be in close proximity for the NO_x reduction reaction to occur at 300 °C, and placing two separate In_2O_3 and Al_2O_3 catalysts in series would not give any NO_x conversion with DME at this temperature. Possibly, the improved NO_x conversion over the In_2O_3-promoted Al_2O_3 catalysts may be associated with distinct active sites at the boundary between In_2O_3 and Al_2O_3-phases.

Based on these observations, the promoting effect on the NO_x conversion reaction when In_2O_3 is added to Al_2O_3 could come from the creation of a more efficient reaction path or from the creation of additional or more active reaction sites, e.g. at the In_2O_3-Al_2O_3 interface. In the first case, the rate determining step in the reaction on Al_2O_3 is bypassed by a reaction on the In_2O_3 surface, but the In_2O_3 surface in itself is inefficient in producing or converting essential reaction intermediates for this alternative reaction path. In order for the overall reaction to proceed certain reaction steps thus need to occur on the Al_2O_3 surface. In the second proposal, the presence of an In_2O_3 interface generates new reaction sites, or alters the electronic structure of sites on the Al_2O_3 surface making them more reactive. A third possibility is that In_2O_3 consumes a species, which would otherwise inhibit the reaction. The mechanistic aspects of the promoting effect of In_2O_3 on Al_2O_3 will be studied with in situ DRIFT spectroscopy and covered in a separate study.

A comparison of the NO_x and DME conversion over the Ga_2O_3/Al_2O_3 catalysts during the steady-state experiments is shown in Fig. 3. The traces for the pure Al_2O_3 catalyst are also included in these graphs for comparison. The Ga_2O_3/Al_2O_3 catalysts showed a higher NO_x conversion than the pure Al_2O_3 catalyst up to about 450 °C. The maximum NO_x conversion of 43% was obtained at 400 °C over the 8.2% Ga_2O_3/Al_2O_3 catalyst. At both 350 and 400 °C this catalyst showed the highest NO_x conversion, but on the other hand it gave the lowest NO_x conversion at temperatures between 450 and 550 °C. The influence of the Ga_2O_3-loading on NO_x conversion was relatively small within the range studied. Above 450 °C the difference between the Ga_2O_3-promoted samples and pure Al_2O_3 was low. In contrast to the In_2O_3/Al_2O_3 catalysts, the Ga_2O_3/Al_2O_3 catalysts were not active at 300 °C. The NO_x conversion over these catalysts showed a temperature dependence more similar to that of the pure Al_2O_3 catalyst. Similar results have been reported with propene as reducing agent over In_2O_3/Al_2O_3 and Ga_2O_3/Al_2O_3 [30].

Regarding the conversion of DME, results were similar for the Ga_2O_3/Al_2O_3 catalysts as for the pure Al_2O_3 catalyst, with the

exception that at lower temperatures, mainly at 300 °C, the catalyst with the highest Ga_2O_3 loading (8.2%) showed a higher DME conversion than the other catalysts. Complete conversion of DME was reached for all catalysts at 400 °C and above.

Fig. 4 shows results from the steady-state experiments of NO_x and DME conversion over B_2O_3/Al_2O_3 and pure Al_2O_3 catalysts at temperatures between 250 and 550 °C. The B_2O_3-promoted alumina catalysts showed a higher NO_x conversion than the pure Al_2O_3 catalyst, at least up to 500 °C. At 550 °C the NO_x conversion was relatively similar for all catalysts in this series. The highest NO_x conversion of 51% was obtained at 400 °C over the catalyst with the lowest B_2O_3-loading (0.30%). This catalyst showed the highest activity between 350 and 450 °C. In this temperature range, the influence of the B_2O_3-loading on NO_x conversion was relatively large, with a maximum difference of 28%-units between the highest and lowest B_2O_3-loaded material. At higher temperatures, i.e. 500 and 550 °C, the 0.76- and 3.0% B_2O_3/Al_2O_3 catalysts showed the highest NO_x reduction, but the differences were smaller. In similarity with Ga_2O_3/Al_2O_3, the B_2O_3/Al_2O_3 catalysts were not active at 300 °C and the NO_x conversion over these catalysts showed a temperature dependence more similar to the pure Al_2O_3 catalyst.

Regarding the DME conversion, results were similar for the B_2O_3/Al_2O_3 catalysts and the pure Al_2O_3 catalyst, with the exception that at lower temperatures (300 and 350 °C), the catalyst with the lowest B_2O_3 loading (0.30%) showed a higher DME conversion than the other catalysts. Thus, for both Ga_2O_3- and B_2O_3-promoted Al_2O_3 the catalysts with the highest NO_x conversion at low temperatures also gave a higher conversion of DME at low temperatures. It is thus likely that the higher NO_x conversion is connected to an increased oxidation ability of these catalysts. Complete conversion of DME was reached for all B_2O_3/Al_2O_3 catalysts at 400 °C and above.

Although pure Ga_2O_3 or B_2O_3 catalysts were not included in this study, it is likely that these, in similarity to pure In_2O_3, are not active for NO_x reduction with DME. In an earlier study pure Ga_2O_3 was reported inactive for NO_x reduction with CH_4, while Ga_2O_3 supported on Al_2O_3 was active [31].

Temperature ramp experiments

In order to investigate in more detail the temperature dependence of the different catalysts, the activity and by-product formation over the catalysts were studied during temperature ramps from 550 to 200 °C. Because DME is known to undergo gas phase reactions in the presence of oxygen [19,20], the conversion
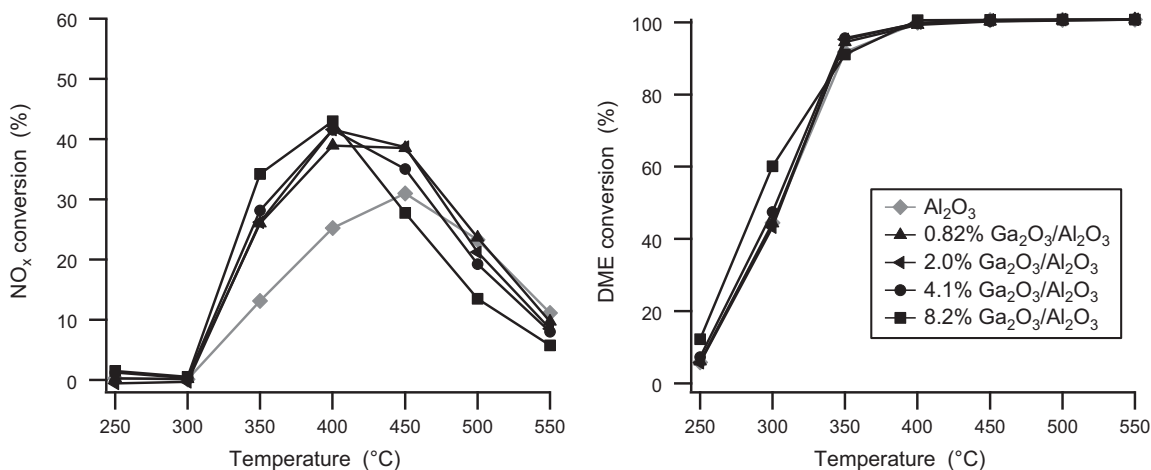
Fig. 3. Conversion of NO_x and DME during steady-state experiments with Ga_2O_3/Al_2O_3 and pure Al_2O_3 catalysts. Gas feed contained 500 ppm NO, 1000 ppm DME, 5% H_2O, 8% O_2, and Ar as balance. Space velocity = 33,400 h^{-1}.

of DME in the empty reactor was investigated initially. Results from this experiment both in the absence (solid lines) and presence (dotted lines) of 5% H_2O in the feed are shown in Fig. 5. Similar results were achieved in both cases, although the on-set of the reactions shifted to a slightly higher temperature in the presence of H_2O. At 340 °C, 80% conversion of DME was achieved in the empty reactor. The reactions led to an almost complete conversion of NO to NO_2. Some CO, formaldehyde, and formic acid were also formed, but the yield of methanol and CH_4 was very low (1% or below, not shown). Interestingly, the conversion of NO_x in the empty reactor reached about 15%. However, the FTIR measurements showed that nitric acid was produced simultaneously with the NO_x conversion. Although exact quantification of the formed nitric acid was not possible, because the calibration curves available for this component were obtained at a different temperature of the FTIR instrument than used in the present study, it is most likely that the observed NO_x conversion was due to the formation of nitric acid.

The reactions of DME in the gas phase are radical reactions and have been investigated in detail by Dagaut et al. [44] and in relation to DME-SCR by Tamm et al. [19,20]. Our observations are in good agreement with those studies. When discussing the results in the remainder of this study it is important to bear in mind the empty reactor data because gas phase reactions will occur to some extent

in the reactor tube before the catalyst and change the composition of the gas reaching the catalyst.

Catalytic performance of In_2O_3/Al_2O_3

The results from temperature ramp experiments in the absence of H_2O in the feed over the In_2O_3/Al_2O_3, pure Al_2O_3, and In_2O_3 catalysts are shown in Fig. 6. When using NO in the feed a maximum of 67% NO_x conversion was obtained at 305 °C over the 12% In_2O_3/Al_2O_3 catalyst, whereas for pure Al_2O_3 the maximum was 49% at 365 °C. When comparing the light-off temperature for NO_x conversion over these two catalysts, it is clear that the addition of In_2O_3 to Al_2O_3 decreased the light-off temperature by about 75 °C, but gave a narrower active temperature window. With decreased In_2O_3-loading from 12 to 1.2% the maximum NO_x conversion gradually decreased and the NO_x conversion curve shifted to higher temperatures. The NO_x- and DME conversion curves follow each other and start to increase at about the same temperature. At the temperature where the maximum in NO_x conversion was achieved the DME conversion was about 90%.

For the pure Al_2O_3 sample both the NO_x- and DME conversion started around the same temperature as where the gas phase reactions of DME started in the empty reactor experiments. The In_2O_3-promoted catalysts, however, started to reduce NO_x at a
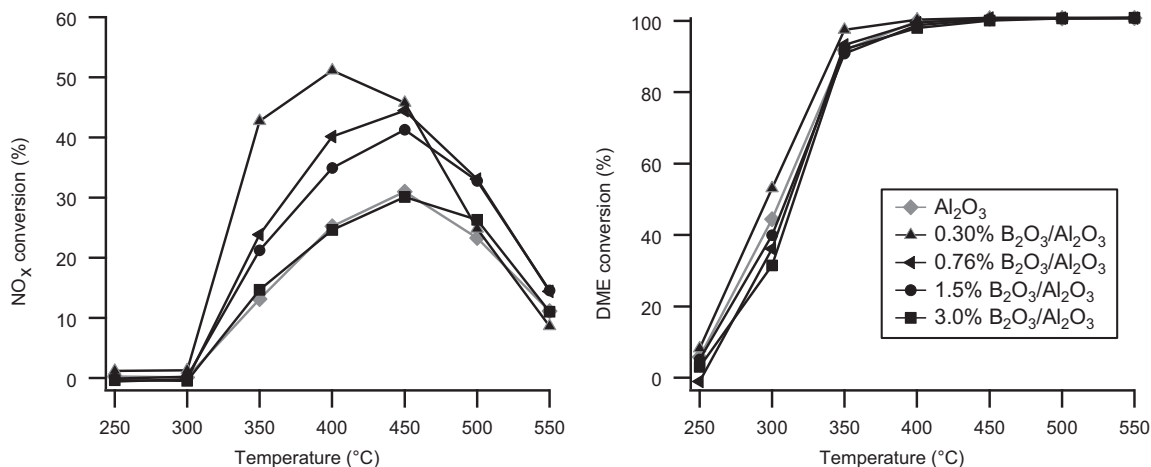

Fig. 4. Conversion of NO_x and DME during steady-state experiments with B_2O_3/Al_2O_3 and pure Al_2O_3 catalysts. Gas feed contained 500 ppm NO, 1000 ppm DME, 5% H_2O, 8% O_2, and Ar as balance. Space velocity = 33,400 h^{-1}.
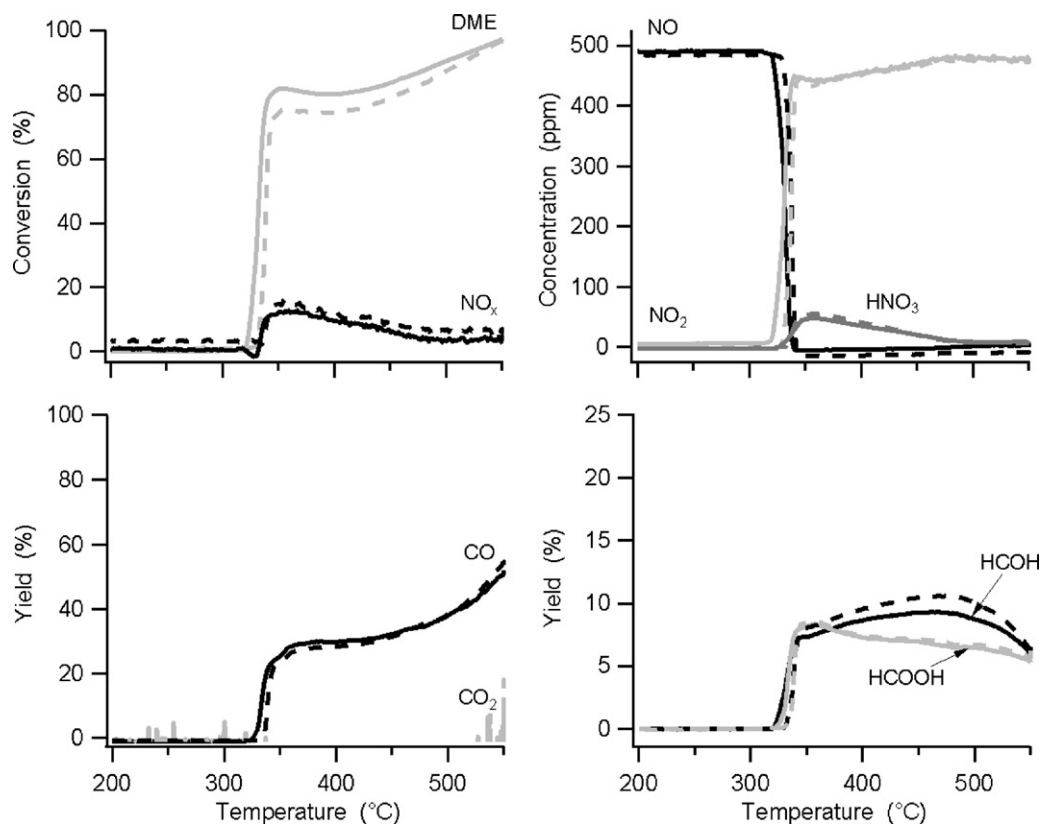
Fig. 5. Conversion of DME and NO_x, and formation of various gases during temperature ramp experiments from 550 to 200 °C in the empty reactor in the absence (solid lines) or presence (dotted lines) of 5% H_2O in the feed. Gas feed contained 500 ppm NO, 1000 ppm DME, 8% O_2, and Ar as balance. Space velocity = 33,400 h^{-1}.

lower temperature and gave only a small shoulder on the NO_x conversion curve around the temperature where the gas phase reactions started. This indicates that the NO_2 formed in the gas phase reactions promoted the NO_x reduction over pure Al_2O_3, as has previously been reported [19], whereas the NO_x reduction over In_2O_3/Al_2O_3 did not rely on the gas phase formation of NO_2. Similarly, the conversion of DME occurred at a lower temperature over the In_2O_3/Al_2O_3-catalysts compared to in the empty reactor, but the DME conversion curves also show a shoulder around the temperature where the gas phase reactions start. Over the pure Al_2O_3 sample, DME was converted at a higher temperature than over In_2O_3/Al_2O_3, but at a lower temperature than over pure In_2O_3. For both the In_2O_3/Al_2O_3- and pure Al_2O_3 catalysts, DME conversion was higher than in the empty reactor and reached 100% at around 350 °C. DME oxidation occurred at a lower temperature with increased In_2O_3-loading. It has previously been reported that oxidation properties are associated with In_2O_3 phases and a shift in the oxidation of hydrocarbons and alcohols to lower temperatures with increased In_2O_3-loading [23,25,28]. Park et al. suggested that well-dispersed In_2O_3 species at low concentrations promote the lean NO_x reduction reaction via partial oxidation and activation of hydrocarbons, whereas high concentrations of In_2O_3 decrease the NO_x reduction activity by blocking active alumina sites [25]. However, for DME the activation through partial oxidation may not be as important. Instead, the increase in NO_x conversion could be a secondary effect connected to an increased oxidation ability of the catalysts.

The CO yield was lower and the CO_2 yield higher over the studied catalysts compared to the empty reactor, but a peak in CO was observed around the temperature where the gas phase reactions started. The NO_2 concentration was very low in the presence of the In_2O_3/Al_2O_3 catalysts, which thus convert the NO_2 produced in

the gas phase above 320 °C back to NO. Over the pure Al_2O_3 catalyst a steady increase in NO_2 slip was observed between 350 and 550 °C.

Consistent with the results from the steady-state experiments, the pure In_2O_3 catalyst was completely inactive for NO_x reduction over the entire temperature range studied. Even when DME became oxidised no NO_x was reduced over In_2O_3. In fact, the DME conversion curve over this catalyst is similar to that of the non-catalytic reaction in the empty reactor, not reaching full conversion until around 550 °C. However, NO_x conversion and nitric acid production were negligible indicating that the nitric acid produced in the gas phase reactions was converted to NO_x over In_2O_3. Studying the NO and NO_2 curves it is interesting to note that, despite showing no NO_x conversion, even the pure In_2O_3 catalyst converted all NO_2 produced in the gas phase back to NO.

With NO_2 in the feed instead of NO, the maximum NO_x conversion increased and reached 80% over the 12% In_2O_3/Al_2O_3 catalyst. Furthermore, some NO_x conversion was achieved already at 200 °C, but the difference in light-off temperature was relatively small. Thus, the NO_x reduction appears in this case to some extent limited by the oxidation of NO to NO_2 at low temperatures. It has previously been reported that over pure Al_2O_3 with propene, the NO_x conversion is increased and shifted to lower temperatures when replacing NO by NO_2 [45,46]. However, at higher temperatures in the current experiments, mainly NO_2 will reach the catalyst even with NO in the feed, due to the gas phase reactions between DME, O_2 and NO, and the difference in NO_x conversion with NO or NO_2 is smaller. Furthermore, the NO_x conversion over In_2O_3/Al_2O_3 catalysts is highly limited by the amount of reducing agent at these temperatures. The DME conversion was similar when using either NO or NO_2 in the feed. Thus, NO_2 was not promoting the DME oxidation and possible activation over this catalyst.
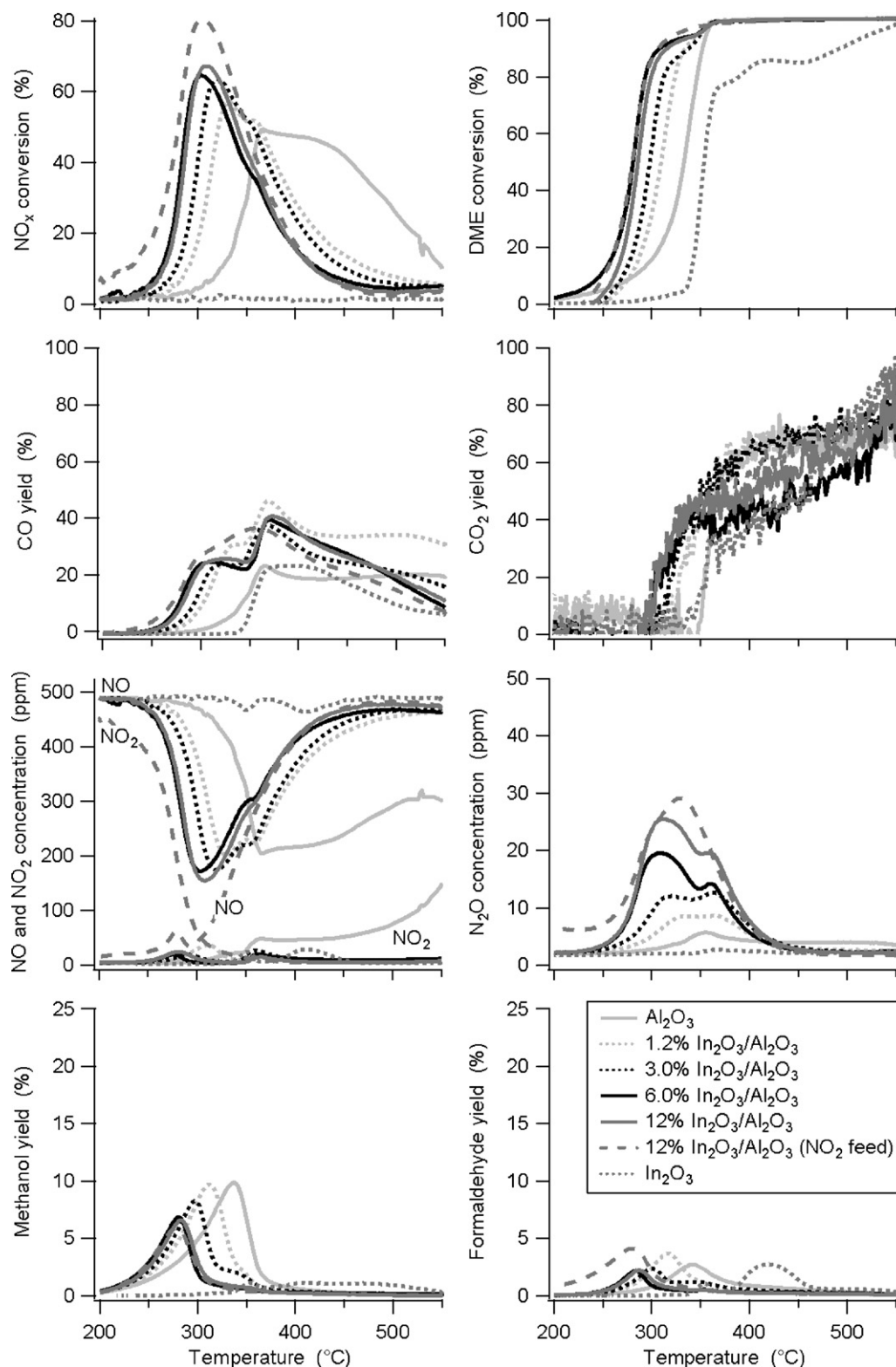
Fig. 6. Catalytic activity test of In_2O_3/Al_2O_3 and pure Al_2O_3 and In_2O_3 catalysts during temperature ramp experiments from 550 to 200 °C. Gas feed contained 500 ppm NO or NO_2, 1000 ppm DME, 8% O_2, and Ar as balance. Space velocity = 33,400 h^{-1}.

The formation of N_2O was negligible over the pure Al_2O_3 catalyst, but increased with In_2O_3 loading. The N_2O curves follow the temperature-dependence of the NO_x conversion curves and the highest N_2O concentration was produced over the catalyst with highest In_2O_3 loading, and increased when NO_2 was used in the feed gas. Thus, there is a loss in selectivity for N_2 formation

associated with increased In_2O_3 loading. The yield of methanol was low, but not negligible, over the In_2O_3/Al_2O_3 and pure Al_2O_3 catalysts and peaked where the DME conversion levels out. Over the pure In_2O_3 catalyst the methanol yield was negligible similar to the empty reactor experiments. In contrast to the empty reactor experiments, the formic acid and nitric acid emissions were

negligible (not shown) and formaldehyde emissions low in the presence of any of the catalysts.

Fig. 7 shows the results from temperature ramp experiments over In_2O_3/Al_2O_3 and pure In_2O_3- and Al_2O_3 catalysts in the presence of H_2O. The higher maximum conversion obtained in these experiments compared to the steady-state experiments is likely due to that the optimum temperature for the catalysts was in between two of the temperatures chosen for steady-state experiments, but could also be partly due to transient effects during the temperature ramps. Comparing Figs. 6 and 7, it is clear that a lower maximum NO_x conversion is obtained in the presence of H_2O. The difference for the In_2O_3/Al_2O_3 catalysts was about 5–20%-units, and about 15% for the pure Al_2O_3 sample. The 3% In_2O_3/Al_2O_3 catalyst was the least sensitive to inhibition by H_2O. The NO_x conversion curves were also shifted to a slightly higher temperature in the presence of H_2O. Furthermore, the influence of the In_2O_3 loading was lower and the 3.0% In_2O_3/Al_2O_3 catalyst now showed the highest NO_x conversion, whereas the 6.0 and 12% In_2O_3/Al_2O_3 catalysts gave the lowest. The DME conversion for the In_2O_3-promoted samples was also shifted to a slightly higher temperature, although for the pure Al_2O_3 catalyst there was an opposite effect, in the presence of H_2O. In fact, the DME conversion curve for the In_2O_3/Al_2O_3 catalysts and pure Al_2O_3 catalyst follow each other well, although it was only over In_2O_3/Al_2O_3 that DME reduced NO below 350 °C. The CO_2 yield was lower, and CO- and methanol yields were higher in the presence of H_2O. Thus, H_2O inhibited the complete oxidation to CO_2 to some extent. The methanol yield was especially large over the pure Al_2O_3 catalyst and decreased with the amount of In_2O_3 added. It is likely that the DME that was converted over the pure Al_2O_3 catalyst below 350 °C produced methanol as the curves of DME conversion and methanol yield follow each other well. Methanol production is expected as Al_2O_3 catalyses the hydrolysis of DME to methanol according to Reaction (1) above about 300 °C [47,48].

$$H_3C-O-CH_3 + H_2O \leftrightarrow 2H_3COH \qquad (1)$$

The reaction is promoted by high acidity of the catalyst and adding In_2O_3 to Al_2O_3 reduces the acidity [34,49]. Additionally, the reduced methanol formation over In_2O_3/Al_2O_3 catalysts could be due to that it was consumed by oxidation with O_2 or NO_x over these catalysts at lower temperatures (around 300 °C) than over pure Al_2O_3 [30]. Above 350 °C the methanol yield decreased further, as the gas phase oxidation of DME reduced the amount of DME present. Over pure In_2O_3 no methanol was formed.

A similar experiment with doubled DME concentration ($HC_1/NO_x = 8$) gave an increase in maximum NO_x conversion by 10–15%-units and a slight shift to lower temperature (not shown). This temperature shift may partly be explained by an increase in catalyst temperature from the reaction heat of DME oxidation.

Catalytic performance of Ga_2O_3/Al_2O_3

The results from temperature ramp experiments in the absence of H_2O over the Ga_2O_3/Al_2O_3 catalysts are shown in Fig. 8 in comparison to pure Al_2O_3. When using NO in the feed a maximum of 56% NO_x conversion was obtained at 360 °C or 370 °C for the 2.0 and 8.2% Ga_2O_3/Al_2O_3 catalysts, respectively. Thus, a somewhat higher maximum NO_x conversion was obtained with Ga_2O_3/Al_2O_3, but with a similar temperature window as pure Al_2O_3. Thus, addition of Ga_2O_3 to Al_2O_3 did not have the same effect on the light-off temperature for NO_x reduction as addition of In_2O_3. The influence of Ga_2O_3-loading on the NO_x conversion was limited within the range studied, although the curve for the 8.2% Ga_2O_3/Al_2O_3 catalyst showed a different behaviour compared to the other Ga_2O_3/Al_2O_3 catalysts. This catalyst started to reduce NO_x at the lowest temperature, has a shoulder on the NO_x conversion curve, reached

maximum conversion at a somewhat higher temperature, but also lost the conversion faster than the other catalysts at higher temperature. DME conversion also started at a slightly lower temperature over the 8.2% Ga_2O_3/Al_2O_3 catalyst compared to the other Ga_2O_3/Al_2O_3 catalysts. In similarity to pure Al_2O_3, DME was completely converted at around 350 °C for all the Ga_2O_3/Al_2O_3 catalysts. The CO yield was higher and CO_2 yield lower over Ga_2O_3/Al_2O_3 catalysts compared to pure Al_2O_3. Also the CO yield showed a different trend for the 8.2% Ga_2O_3/Al_2O_3 sample, where CO was released at a lower temperature compared to the other samples. This catalyst was apparently able to oxidise and activate the hydrocarbon at a lower temperature than the other catalysts. Similar to pure Al_2O_3, the Ga_2O_3/Al_2O_3 catalysts showed a considerable NO_2 slip above 350 °C.

With NO_2 in the feed instead of NO over 8.2% Ga_2O_3/Al_2O_3, the NO_x conversion increased over the entire temperature range. The maximum NO_x conversion reached 73% and was shifted to a lower temperature (320 °C). Furthermore, about 15% NO_x conversion was achieved already at 200 °C with NO_2. Thus, the NO_x reduction was to some extent limited by the oxidation of NO to NO_2 at low temperature. Above the temperature where the gas phase reactions of DME start to occur (ca 320 °C) mainly NO_2 will reach the catalyst also with NO in the feed. The reason for the increased NO_x conversion with NO_2 at these temperatures is most likely that it limits the gas phase oxidation of DME, and thus more DME will be accessible for the NO_x reduction [20]. The DME conversion was also shifted to a lower temperature when using NO_2 in the feed instead of NO. This indicates that NO_2 formation may be important for DME activation over this catalyst.

The formation of N_2O was negligible over all catalysts, except for the experiment with NO_2 in the feed, where some N_2O was produced at temperatures below 350 °C. This could be expected as N_2O is generally formed during NO_x reduction at low temperatures and the experiment with NO_2 is the only one where NO_x conversion was achieved between 200 and 300 °C. The yield of methanol over Ga_2O_3/Al_2O_3 was similar to that over pure Al_2O_3. The formic acid (not shown) and formaldehyde emissions were negligible over the Ga_2O_3/Al_2O_3 catalysts with NO in the feed. With NO_2 in the feed there was a slightly higher formaldehyde yield at low temperatures.

Fig. 9 shows the results from temperature ramp experiments over Ga_2O_3/Al_2O_3 and pure Al_2O_3 catalysts in the presence of H_2O. A lower maximum NO_x conversion was obtained in the presence of H_2O than in its absence. The difference was larger for pure Al_2O_3 than for the Ga_2O_3/Al_2O_3 catalysts. Thus, addition of Ga_2O_3 to Al_2O_3 made it less susceptible to inhibition by H_2O in the feed. The NO_x conversion curves were also shifted to a slightly higher temperature in the presence of H_2O, especially for the 8.2% Ga_2O_3/Al_2O_3 catalyst, whose shoulder on the NO_x conversion curve also disappeared in the presence of H_2O, indicating that one of the concurrent processes occurring on this catalyst was inhibited by H_2O. The shift to higher temperature is likely due to that the gas phase reactions of DME shifted to higher temperature in the presence of H_2O as shown in Fig. 5. Interestingly, the DME conversion over the Ga_2O_3-promoted catalysts shifted to slightly lower temperature in the presence of H_2O in similarity to over pure Al_2O_3. This is in accordance with previously reported results by Miyahara et al. [27] over Ga_2O_3/Al_2O_3 with DME. In that study, the conversion of alkanes or alkenes, on the other hand, was shifted to higher temperatures in the presence of H_2O. Thus, addition of H_2O promoted DME conversion over Ga_2O_3/Al_2O_3 and pure Al_2O_3 catalysts, but not over In_2O_3/Al_2O_3. As discussed for pure Al_2O_3 above, the DME that is converted likely produced methanol according to Reaction (1), because the curves of DME conversion and methanol yield follow each other well. The methanol yield was much higher in the presence of H_2O and similar over Ga_2O_3/Al_2O_3 and pure Al_2O_3 catalysts. Thus, Ga_2O_3/Al_2O_3 catalysts in similarity to pure Al_2O_3 are relatively active catalysts

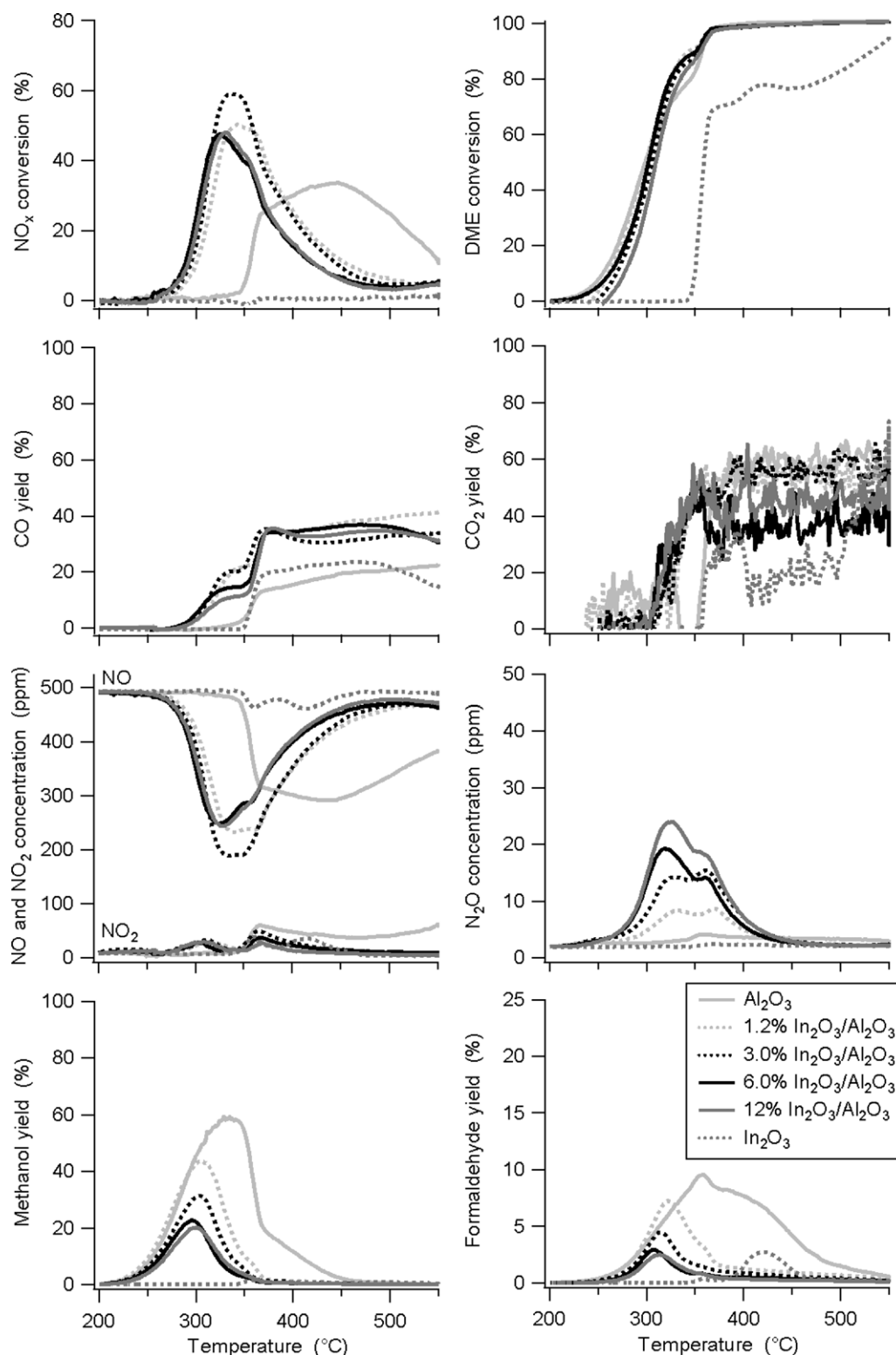**Fig. 7.** Catalytic activity test of In_2O_3/Al_2O_3 and pure Al_2O_3 and In_2O_3 catalysts during temperature ramp experiments from 550 to 200 °C in the presence of H_2O. Gas feed contained 500 ppm NO, 1000 ppm DME, 8% O_2, 5% H_2O, and Ar as balance. Space velocity = 33,400 h^{-1}.

for the hydrolysis of DME to methanol. Additionally, it is plausible that Ga_2O_3/Al_2O_3 is not so active for methanol oxidation with O_2 or NO_x at low temperatures (around 300 °C), in similarity to pure Al_2O_3. The CO_2 yield was lower and CO yield slightly higher in the presence of H_2O at higher temperatures. Formaldehyde yield was higher in the presence of H_2O and similar over the Ga_2O_3/Al_2O_3

and pure Al_2O_3 catalysts, whereas formic acid yield (not shown) and N_2O formation were still negligible.

A similar experiment with doubled DME concentration ($HC_1/NO_x = 8$) gave an increase in maximum NO_x conversion by 10–15%-units and a slight shift to lower temperature (not shown). In particular, the NO_x conversion at high temperature,
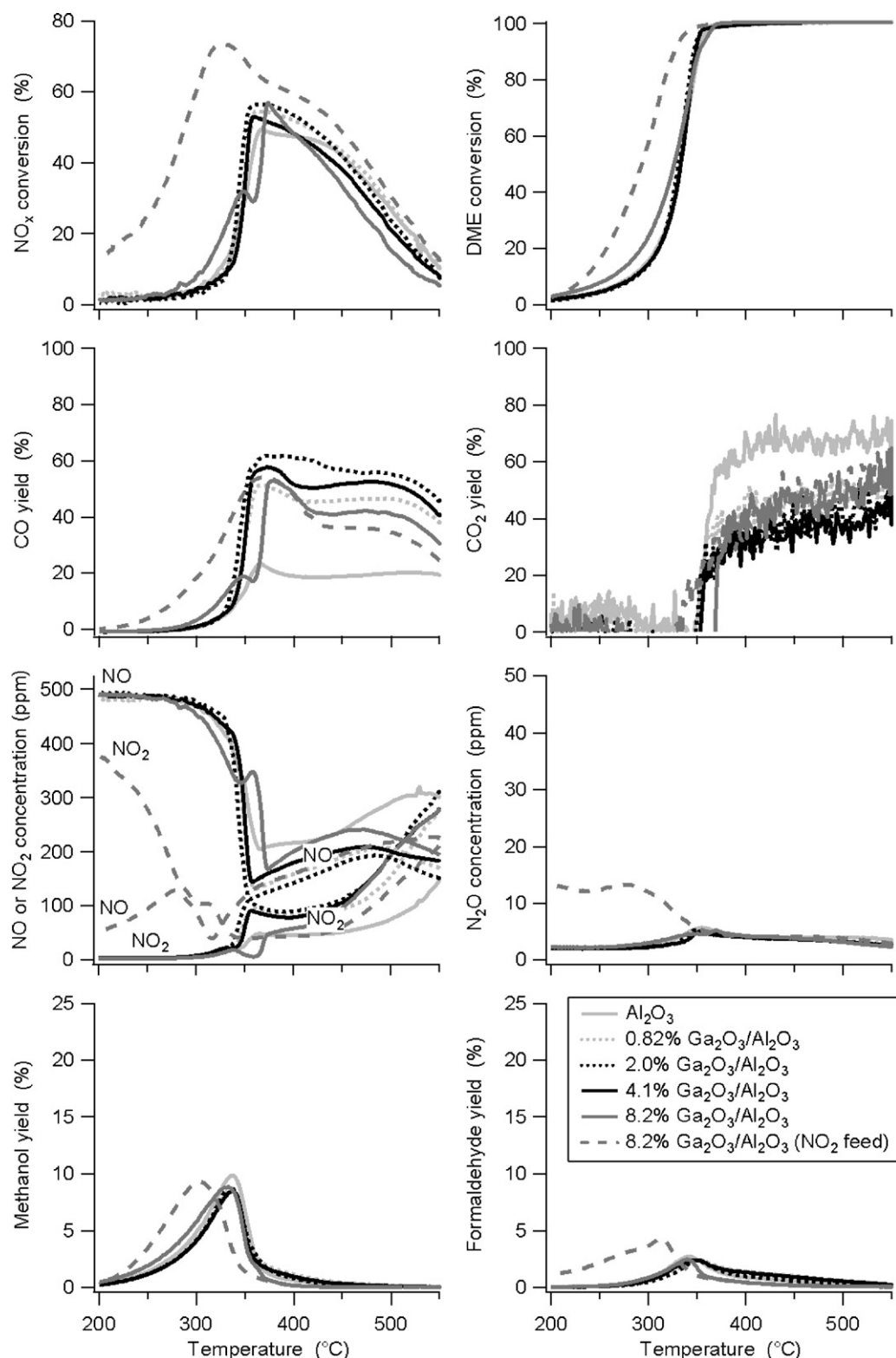
Fig. 8. Catalytic activity test of Ga_2O_3/Al_2O_3 and pure Al_2O_3 catalysts during temperature ramp experiments from 550 to 200 °C. Gas feed contained 500 ppm NO or NO_2, 1000 ppm DME, 8% O_2, and Ar as balance. Space velocity = 33,400 h^{-1}.

where it is limited by the amount of reducing agent available, was considerably increased, over the Ga_2O_3/Al_2O_3 catalysts. This was not observed over the In_2O_3/Al_2O_3 catalysts, which is likely due to that over these catalysts all DME was consumed by oxidation with oxygen even at doubled DME concentration due to the higher oxidation ability of this catalyst. The decrease in light-off temperature for NO_x conversion is consistent with the results by Tamm

et al. [20], showing that the gas phase reaction of DME and NO was shifted to lower temperatures with increased DME/NO_x ratio.

Catalytic performance of B_2O_3/Al_2O_3

The results from temperature ramp experiments in the absence of H_2O over B_2O_3/Al_2O_3 catalysts are shown in Fig. 10 in comparison to pure Al_2O_3. When using NO in the feed a maximum of 67%

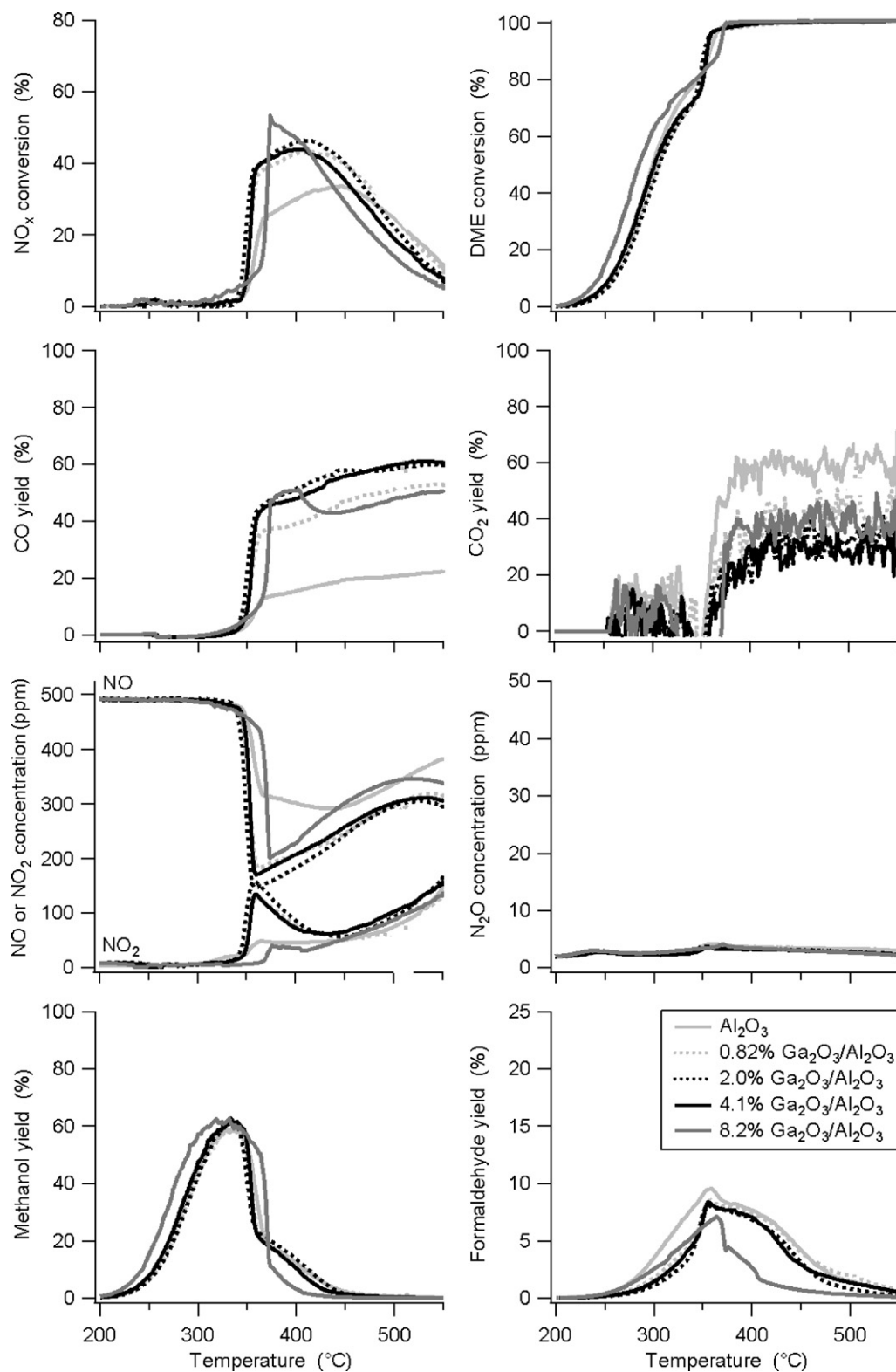**Fig. 9.** Catalytic activity test of Ga_2O_3/Al_2O_3 and pure Al_2O_3 catalysts during temperature ramp experiments from 550 to 200 °C in the presence of H_2O. Gas feed contained 500 ppm NO, 1000 ppm DME, 8% O_2, 5% H_2O, and Ar as balance. Space velocity = 33,400 h^{-1}.

NO_x conversion was obtained at 355 °C for the 0.30% B_2O_3/Al_2O_3 catalyst. This is the same degree of conversion as the maximum observed with In_2O_3/Al_2O_3, although for that catalyst at about 50 °C lower temperature. Thus, a higher maximum in NO_x conversion was obtained over B_2O_3/Al_2O_3 compared to both Ga_2O_3/Al_2O_3 and pure Al_2O_3, but with a similar temperature window. The influence

of B_2O_3 loading on the NO_x conversion was larger than for Ga_2O_3 and In_2O_3, and showed the opposite trend, because the catalyst with the lowest B_2O_3 loading (0.30%) showed the highest maximum NO_x conversion, which then gradually decreased with increased B_2O_3 loading. In addition, the 0.30% B_2O_3/Al_2O_3 catalyst started to reduce NO_x at the lowest temperature. The DME conversion
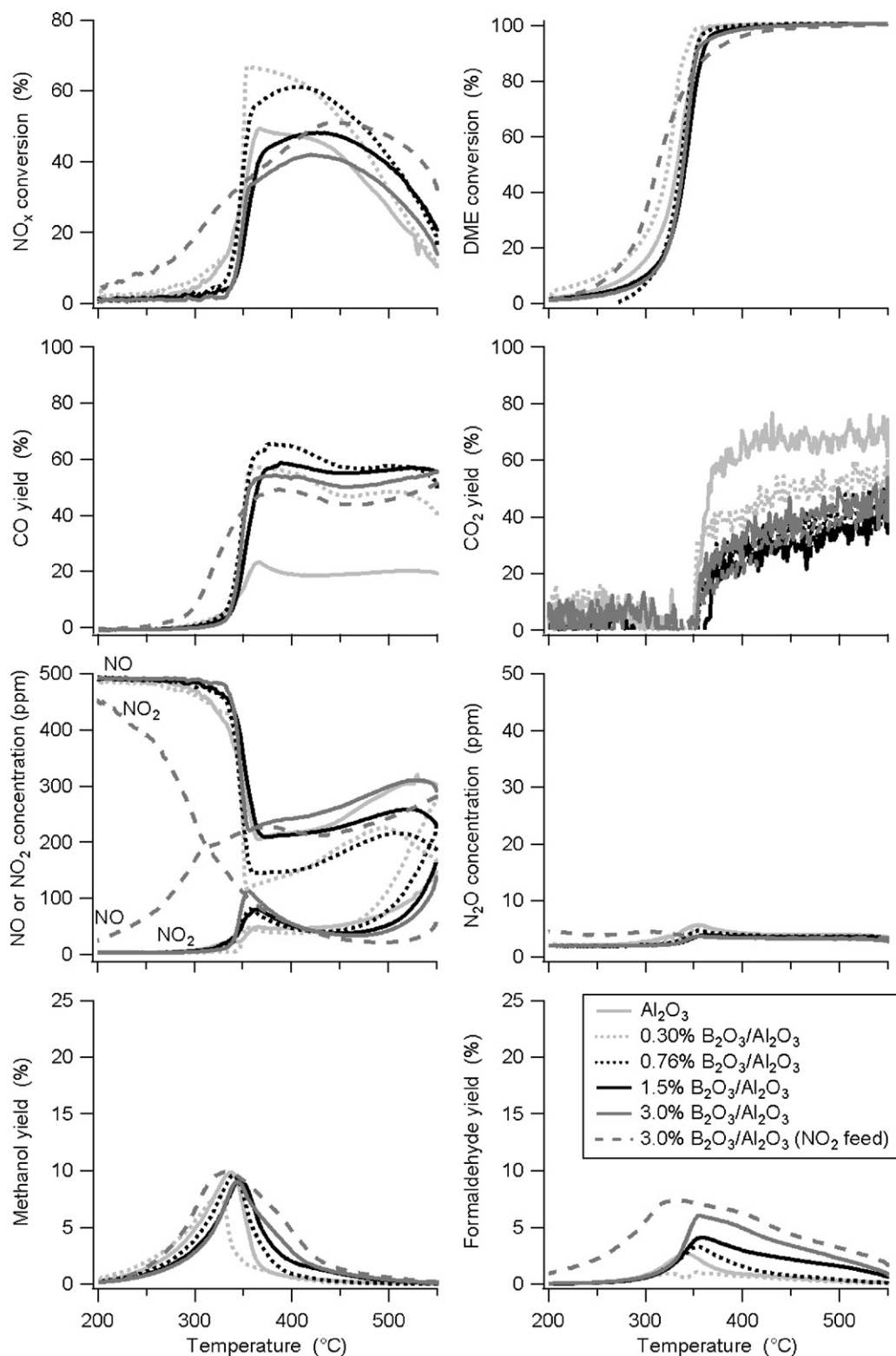
Fig. 10. Catalytic activity test of B_2O_3/Al_2O_3 and pure Al_2O_3 catalysts during temperature ramp experiments from 550 to 200 °C. Gas feed contained 500 ppm NO or NO_2, 1000 ppm DME, 8% O_2, and Ar as balance. Space velocity = 33,400 h^{-1}.

also started at the lowest temperature over the 0.30% B_2O_3/Al_2O_3 catalyst compared to over the other B_2O_3/Al_2O_3- and pure Al_2O_3 catalysts. Similar to pure Al_2O_3, DME was completely converted at around 350 °C for all the B_2O_3/Al_2O_3 catalysts and these catalysts also showed a considerable NO_2 slip above 350 °C, which was the highest for 0.30% B_2O_3/Al_2O_3. As was the case for the Ga_2O_3/Al_2O_3

catalysts, the CO yield was higher and the CO_2 yield lower over the B_2O_3/Al_2O_3 catalysts compared to pure Al_2O_3.

With NO_2 in the feed instead of NO over the 3.0% B_2O_3/Al_2O_3 catalyst, the NO_x conversion increased over the entire temperature range, but especially at low temperature. Thus, the NO_x reduction was to some extent limited by the oxidation of NO to NO_2 at low
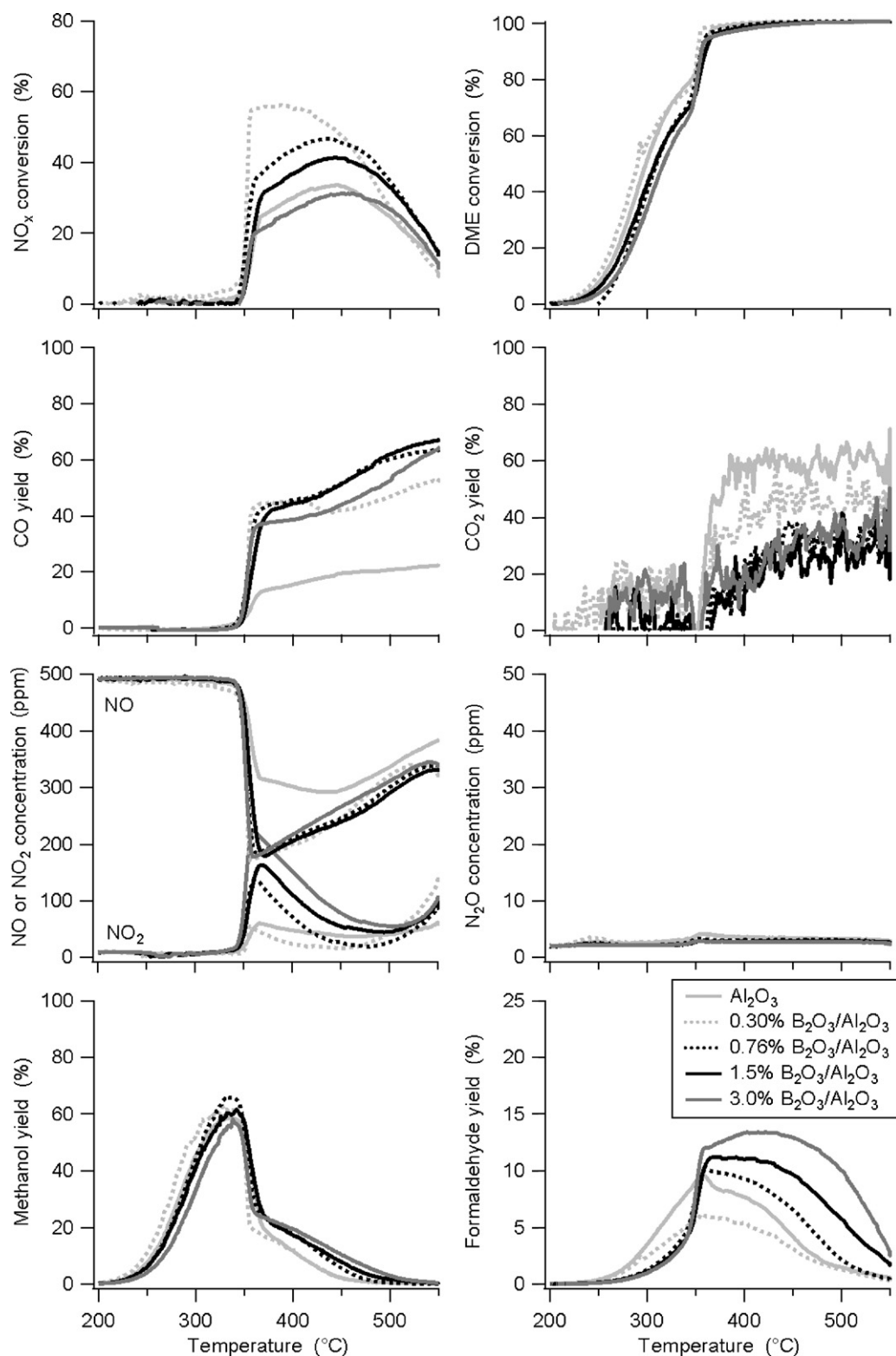
Fig. 11. Catalytic activity test of B_2O_3/Al_2O_3 and pure Al_2O_3 catalysts during temperature ramp experiments from 550 to 200 °C in the presence of H_2O. Gas feed contained 500 ppm NO, 1000 ppm DME, 8% O_2, 5% H_2O, and Ar as balance. Space velocity = 33,400 h^{-1}.

temperature. As mentioned for Ga_2O_3/Al_2O_3, above the temperature where the gas phase reactions of DME started (ca 320 °C) the reason for the increased NO_x conversion with NO_2 is most likely that it inhibits the gas phase oxidation of DME, and thus more DME will be accessible for NO_x reduction [20]. The DME conversion was also shifted to a lower temperature when using NO_2 in the feed

instead of NO. This indicates that NO_2 may be important for DME activation over this catalyst.

With both NO and NO_2 in the feed the formation of N_2O was negligible over the B_2O_3/Al_2O_3 catalysts, indicating a high selectivity to N_2. The yield of methanol over B_2O_3/Al_2O_3 was similar to that over the pure Al_2O_3 catalyst. The formic acid (not shown)

emissions were negligible and formaldehyde emissions low over B_2O_3/Al_2O_3 with NO in the feed. With NO_2 in the feed, there was a slightly higher formaldehyde yield at lower temperatures, similar to the corresponding experiment with Ga_2O_3/Al_2O_3.

Fig. 11 shows the results from temperature ramp experiments over B_2O_3/Al_2O_3- and pure Al_2O_3 catalysts in the presence of H_2O. A lower maximum NO_x conversion was obtained in the presence of H_2O than in its absence. The difference was larger for the pure Al_2O_3 sample than for the B_2O_3/Al_2O_3 catalysts. Thus, similar to Ga_2O_3, addition of B_2O_3 to Al_2O_3 made it less susceptible to inhibition by H_2O in the feed. The NO_x conversion curves were also shifted to a slightly higher temperature in the presence of H_2O, especially for the 0.3% B_2O_3/Al_2O_3 sample. As discussed for Ga_2O_3/Al_2O_3 catalysts, this is likely due to that the gas phase reactions of DME shifted to higher temperatures in the presence of H_2O as shown in Fig. 5. The DME conversion for the B_2O_3-promoted samples was shifted to a somewhat lower temperature. As discussed earlier, it is likely that the DME that was converted produced methanol by hydrolysis, because the curves of DME conversion and methanol yield follow each other well. The methanol yield was much higher in the presence of H_2O and similar over the B_2O_3/Al_2O_3 and pure Al_2O_3 catalysts. Thus, B_2O_3/Al_2O_3 catalysts in similarity to the Ga_2O_3/Al_2O_3 and pure Al_2O_3 catalysts are relatively active catalysts for the hydrolysis of DME to methanol. Additionally, it is plausible that Ga_2O_3/Al_2O_3 is not so active for methanol oxidation with O_2 or NO_x at low temperatures (around 300 °C), in similarity to pure Al_2O_3. The CO_2 yield was slightly lower and the CO yield slightly higher in the presence of H_2O at high temperatures. The formaldehyde yield was higher in the presence of H_2O and somewhat higher over the high loaded B_2O_3/Al_2O_3 catalysts compared to pure Al_2O_3, whereas the formic acid yield (not shown) and N_2O formation were still negligible.

Similar to the Ga_2O_3/Al_2O_3 catalysts, an experiment with doubled DME concentration ($HC_1/NO_x = 8$) over B_2O_3/Al_2O_3 gave an increase in maximum NO_x conversion by 10–15%-units and a slight shift to lower temperature (not shown). Furthermore, the NO_x conversion at high temperature, where it is limited by the amount of reducing agent available, was considerably increased, over both catalysts.

In summary, the flow reactor experiments of the In_2O_3-, Ga_2O_3-, and B_2O_3-promoted Al_2O_3 catalysts showed that In_2O_3/Al_2O_3 gave the highest NO_x conversion at low temperatures, but a more narrow active temperature window compared to pure Al_2O_3. Ga_2O_3/Al_2O_3, and B_2O_3/Al_2O_3, on the other hand, gave an active temperature window more similar to pure Al_2O_3, but with a higher NO_x conversion. The Ga_2O_3- and B_2O_3- promoted catalysts did not show the same promoting effect on the light-off temperature for NO_x conversion as the In_2O_3-promoted catalysts, but only increased the maximum NO_x conversion compared to pure Al_2O_3. Thus, it is likely that the promoting effect of Ga_2O_3 and B_2O_3 may have a different origin than the effect of In_2O_3.

The differences between the catalysts activity for NO_x reduction could to some extent be connected to the acidic or basic properties of the oxides. The connection between catalytic activity for NO_x reduction and the surface acidity of solid acid type catalysts like γ-Al_2O_3 has been proven in several studies [12,50,51]. For NO_x reduction with DME, Masters et al. [12] found that the alumina catalyst with highest acidity gave the highest NO_x conversion. Relevant to the present study, Petre et al. [49] studied the surface acidity and basicity of B_2O_3-, Ga_2O_3-, and In_2O_3/Al_2O_3 catalysts by gas phase adsorption microcalorimetry. They found that addition of B_2O_3 to Al_2O_3 increased the acidity, especially the number of sites with weak acidic strength, whereas it demonstrated no real basic properties. On the other hand, at low loadings addition of Ga_2O_3 and In_2O_3 (ca 3 wt%) to Al_2O_3 showed little difference compared to Al_2O_3, except that In_2O_3 decreased the number of basic

sites, whereas at higher loadings (17–25 wt%) they both decreased the number of acidic sites, particularly the sites with medium and strong acidic strength. At high loading the number of acidic sites varied in the order $B_2O_3 > Al_2O_3 > Ga_2O_3 > In_2O_3$, which in some aspects correlate with the NO_x reduction activity found here. Thus, the high activity of the low loaded B_2O_3 for NO_x reduction with DME could be connected to this sample having an optimised balance of the surface acidity. However, when comparing all catalysts no clear trend between the activity and the surface acidity of the different group 13-oxides can be discerned.

Conclusions

The group 13 oxides, In_2O_3, Ga_2O_3, and B_2O_3 supported on γ-alumina were shown to be active catalysts for lean NO_x reduction with DME. At an optimum concentration, all promoters increased the maximum NO_x conversion compared to pure Al_2O_3. Of the catalysts studied, In_2O_3/Al_2O_3 gave the highest activity at lower temperatures and reduced the light-off temperature for NO_x reduction by about 50–100 °C compared to pure alumina. However, In_2O_3/Al_2O_3 gave a narrower active temperature window and a lower NO_x conversion than pure alumina at temperatures above 400 °C. Pure In_2O_3 was found inactive for NO_x reduction with DME. B_2O_3- and Ga_2O_3/Al_2O_3 catalysts, on the other hand, gave a temperature window more similar to pure Al_2O_3, but with higher NO_x conversion. The presence of 5% H_2O in the feed resulted in a lower NO_x conversion over all catalysts, although addition of Ga_2O_3 or B_2O_3 to Al_2O_3 made it less susceptible to inhibition by H_2O.

Regarding the promoting effect of In_2O_3 at lower temperature, it was concluded that a close interaction between In_2O_3 and Al_2O_3 is needed, because In_2O_3 by itself does not affect the gas composition under these conditions. The promoting effect could be due to that In_2O_3 consumes a species which would otherwise inhibit the reaction; come from the creation of a more efficient reaction path; or formation of additional or more active reaction sites.

Acknowledgements

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